

Predictive reactive transport modeling at a proposed uranium in situ recovery site with a general data collection guide

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Abstract

While restoration of uranium in situ recovery (ISR) sites to predevelopment conditions is ideal, this is often very difficult to achieve. Future downgradient groundwater geochemistry can be evaluated using reactive transport modeling coupled with appropriate data collection. Regulatory requirements specify that the geochemistry at the aquifer exemption boundary (compliance point set by the US Environmental Protection Agency) should never be affected, but compliance with this regulation has not been monitored at previous ISR sites. At the Dewey Burdock site near Edgemont, South Dakota, USA, a change in groundwater flow directions has created a scenario in which the oxidized side of a uranium roll-front deposit is downgradient from the ore zone. This creates a greater risk for future uranium transport, since conventional knowledge of uranium geochemistry considers the reducing side as providing more natural attenuation. Reactive transport modeling using uranium sorption parameters from batch sorption tests provides a predictive tool for future uranium transport. Prediction variations are tested using two different samples, different reaction assumptions, and possible pH measurement error. The results indicate a large variation in predictions with a high sensitivity to sorption parameters due to sample heterogeneity, pH changes, and the presence or absence of calcite. While the sample data set for these initial predictions is limited, the results highlight the need for additional calibration points and a thorough understanding of rock/water interactions in the downgradient zone. We provide a general data collection guide for steps in evaluating downgradient transport at future uranium ISR sites. These steps include core sampling in the downgradient zone and the restored zone along with batch sorption and column testing with restored groundwater and evolved background groundwater within the restored zone. Final reactive transport modeling will rely on high-quality calibration data from batch and column testing (plus any available field testing), but thorough site evaluation will also require appropriate long-term monitoring.

Introduction

Background

Sandstone-hosted uranium roll-front deposits are found in Tertiary-age sediments throughout the western United States (Hobday and Galloway 1999). Uranium roll-front deposits form at the interface between oxidized and reduced sandstones (Fig 1). Generally, the original source for the uranium is granitic rocks

or volcanic ash with uranium concentrations slightly greater than crustal abundance. In the presence of oxygen, uranium remains soluble in the groundwater until a reduction front is encountered, where uranium becomes less soluble. These redox fronts are formed down-dip or down-gradient from the recharge area (Fig. 1). The geochemistry associated with these deposits is complex and variable, but overall they contain a mixture of U^{6+} minerals on the oxidized side of the front and U^{4+} minerals on the reduced side of the front [ADDIN EN.CITE

<EndNote><Cite><Author>Harshman</Author><Year>1974</Year><RecNum>16</RecNum><record><rec-number>16</rec-number><foreign-keys><key app="EN" db-id="tzz00fzjps2vqe52edv99s69eet002zzt2z">16</key></foreign-keys><ref-type name="Book Section">5</ref-type><contributors><authors><author>Harshman, E.N.</author></authors></contributors><titles><title>Distribution of elements in some roll-type uranium deposits</title><secondary-title>Formation of Uranium Ore Deposits - Proceedings of a Symposium; Athens, 6-10 May, 1974</secondary-title></titles><pages>169-183</pages><dates><year>1974</year></dates><urls></urls><research-notes>I have a copy of this book - IAEA Proceedings volume - filed with other IAEA publications</research-notes></record></Cite></EndNote>]. Due to sorption or mineral precipitation reactions, uranium concentrations within an ore zone may or may not be above drinking water standards. However, groundwater within uranium roll-front deposits is usually not of drinking water quality, due to high concentrations of uranium daughter products, mainly radium and radon.

The relatively low-grade uranium in these deposits and their location in young, near-surface, permeable sandstones make them economically mineable using in situ recovery (ISR) techniques. Uranium ISR reverses the process that caused them to be deposited. The process involves the addition of oxygen and carbon dioxide or sodium bicarbonate. Oxygen and complexing agents are added to groundwater to form a lixiviant, which is circulated through a well field developed around the rolls, oxidizing uranium from U^{4+} to U^{6+} and dissolving it into groundwater (Fig. 2). The groundwater containing aqueous uranium (pregnant lixiviant) is pumped to the surface, and the uranium is removed from solution in ion exchange tanks. The “barren” lixiviant is then re-fortified with oxygen and a complexing agent to be recirculated through the ISR well field (Fig. 2). Slightly more water is extracted than injected in order to maintain an inward hydraulic gradient to prevent the movement of the lixiviant into portions of the aquifer not targeted for uranium recovery. Once recovery is complete, well fields are generally restored by flushing out the recovery zones using either local or treated groundwater.

Regulatory Requirements and Current Status

The US Environmental Protection Agency (EPA) is tasked under the Safe Drinking Water Act with establishing requirements that protect underground sources of drinking water. Under the Uranium Mill Tailings Radiation Control Act of 1978 (UMTRCA) section 206, EPA is also authorized to develop health and environmental standards for sites where ores are processed for their uranium content. In 1983 (with updates in 1995), EPA promulgated regulations at Title 40 *Code of Federal Regulations* Part 192, “Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings,” in response to the statutory requirements of UMTRCA. When EPA promulgated these standards, uranium recovery was based almost exclusively on the conventional milling process, but since that time, uranium recovery in the United States has shifted to uranium ISR technology. Because of this, the regulations in 40 CFR 192 are not specific to uranium ISR sites, but they have been applied based on the Solid Waste Disposal Act

(EPA 2011 and EPA 2012a). EPA is currently evaluating the regulations in 40 CFR 192 for potential amendments that are specific to uranium ISR facilities (EPA 2011 and EPA 2012a). In a response to a scientific advisory review of the potential amendments (EPA 2012a), the EPA director states, “Your advisory report emphasizes the role that geochemical modeling can play in furthering our understanding of the underlying chemical processes that may control concentration limits and reaction mechanisms responsible for the mobilization of uranium and other metals in the ISL/ISR process. We are currently looking at ways in which geochemical modeling can help inform both establishing and implementing new ISL/ISR standards” (EPA 2012b).

Currently, for uranium ISR to proceed in the United States, the US EPA Underground Injection Control (UIC) program must approve an aquifer exemption request submitted by the state UIC program, which permanently exempts the mineable portion of the aquifer as a future source of drinking water under the Safe Drinking Water Act. This exemption recognizes that the presence of uranium ore makes the groundwater unfit as drinking water. However, private drinking water wells may exist near the permit boundary of proposed ISR sites. Current EPA regulation 40 CFR 144.12 indicates that no impact on groundwater quality can occur beyond the aquifer exemption boundary. In the United States, the Nuclear Regulatory Commission (NRC) or state regulators evaluate final uranium ISR site closure and any longer-term monitoring requirements. In Texas and Wyoming, past closures of uranium ISR sites have only required stability monitoring within the restored area for 6 months to 1 year (NRC 2009, EPA 2011). These sites were often closed based on a “class of use” for groundwater (NRC 2009), which meant that the groundwater within the restored zone was not always restored to pre-ISR conditions for all constituents (Hall 2009). For these sites, no long-term impacts on downgradient groundwater quality were evaluated, and no long-term monitoring was required. Consequently, the EPA requirement of no impact on groundwater quality outside of the aquifer exemption boundary cannot currently be evaluated. However, evaluations of the current permitting requirements are beginning to recognize the need for downgradient modeling as a tool for understanding longer-term groundwater geochemistry (EPA 2011, 2012a, and 2012b).

Reactive Transport Modeling

Given the lack of long-term monitoring data at past ISR sites coupled with difficulties in restoring ISR zones to full pre-mining conditions (Borch et al. 2012, Hall 2009), use of predictive reactive transport modeling is an important tool to alleviate stakeholder concerns and satisfy regulatory requirements. Attenuation of metal contaminants in groundwater has often been addressed using simple retardation approaches (Bethke and Brady 2000). However, reactive transport modeling incorporates important geochemical complexities that are required for more accurate transport predictions (Bethke and Brady 2000; Curtis et al. 2009). These added geochemical complexities are beginning to be recognized as being especially important at ISR sites (EPA 2011, 2012b). This paper focuses on the appropriate use and data requirements for predictive reactive transport modeling in addressing the possible long-term geochemical changes in aquifers downgradient from ISR sites. Reactive transport modeling related to the proposed Dewey Burdock uranium ISR site near Edgemont, South Dakota, USA (Fig. 3) provides an example approach. While this modeling is very site specific, additional data needs are identified and appropriate approaches are provided that should be applicable to any future uranium ISR site. To give a more consistent methodology across uranium ISR sites, a general data collection guide is provided that will help guide the collection of the necessary data for inputs into more accurate reactive transport modeling.

These approaches are generally applicable to any site with potential downgradient metal transport in the groundwater.

Dewey Burdock Study Site

Initial Data

For any proposed uranium ISR site, the initial groundwater data requirements for the permitting process generally include (1) baseline groundwater quality, (2) groundwater flow directions, and (3) aquifer hydraulic conductivities. These data come from company monitoring well installations and subsequent sampling (groundwater quality and hydraulic head measurements). Several aquifer tests might be performed to determine hydraulic conductivities and measure the integrity of confining units. These data are basic first-step information in understanding the site hydrogeology. Such information for the Dewey Burdock site is provided in license/permit applications to the NRC and EPA (Powertech 2009 and Powertech 2008, respectively) and the final NRC Supplemental Environmental Impact Statement (NRC 2014).

In addition to an understanding of the basic hydrogeologic conditions at an ISR site, multiple drilling locations are used to define the uranium roll-front and the associated ore zone. Currently, regulatory requirements do not specifically require the collection of rock core during the permit process. At the Dewey Burdock site, the overall locations of the uranium roll-front deposit, oxidized zones, and reduced zones were mapped using exploration holes with geophysical logging. This logging allowed for the identification of geologic units and the locations of uranium ore zones with gamma logs. In addition, a few confirmation core holes were drilled. The mining company used these cores for ore zone confirmation and ore recovery testing. The remaining, unpreserved core (stored in typical rock core boxes) was also analyzed for additional characterization of the mineralogy (Johnson et al. 2013). Several oxidized core zones were also analyzed for iron content and uranium sorption testing (Johnson et al. [in review]). The results and interpretations from the sorption testing in Johnson et al. (in review) are used as input data in the reactive transport modeling provided in this paper. While the core from the Dewey Burdock site was not directly downgradient from the proposed recovery zones, it provides proxy core information for likely geochemical conditions within the oxidized zone. Some reduced zone core material was also available and was analyzed for sulfur, carbon, and metal content (Johnson et al. 2013). However, the reduced zone core was not kept anoxic, so it was not considered reliable material for the laboratory determination of uranium sorption and precipitation potentials for use in reactive transport modeling.

Evaluation of Downgradient Oxidized Zone

The natural condition for a uranium roll-front is for uranium to be sorbed or precipitated in the reduction front due to the presence of organic carbon or pyrite, or both. At a currently forming roll front (Fig. 1), groundwater uranium concentrations in the oxygenated side should be higher than in the reduced side. At the Dewey Burdock site, the groundwater flow direction during uranium roll-front formation was likely toward the southeast (white arrow in Fig. 4), but the current groundwater flow direction is rotated 90 degrees, with groundwater flow toward the southwest (black arrow in Fig. 4). As a result, much of the groundwater is depleted in oxygen content, even in the oxidized zone (Johnson 2012), because oxygen is depleted in the surrounding, upgradient reduced zone. Uranium concentrations in groundwater across the site, including the ore zone, are low because of this oxygen depletion, which reduces the uranium

solubility. However, uranium daughter products, such as radium and radon, are well above drinking water standards within the ore zone (Powertech 2008).

The uranium ore zones surround the redox boundary, and the black dots in Fig. 4 are previous drill hole locations completed for ore identification. For an evaluation of future groundwater conditions downgradient from proposed ISR zones, the change in groundwater flow conditions at Dewey Burdock create a situation in which the oxidized solid-phase is downgradient from the ore zone for a large portion of the site (Fig. 4). To the authors' knowledge, at ISR sites, a change in groundwater flow direction through geologic time is not unusual, but a full 90 degree difference is unique. In the oxidized zone, core data indicate a lack of pyrite and organic carbon, with the oxidized iron occurring either as amorphous iron oxyhydroxide or as hematite. Up to 1 wt. % hematite was detected in X-ray diffraction analyses (Johnson et al. 2013). The resulting reddish iron within the core is very apparent (Fig. 4). In general, uranium is expected to be less mobile in reducing zones due to a greater potential for uranium precipitation and sorption than in the oxidized zone based on the mineralogy, as this is the controlling mechanism for the original formation of the uranium deposit. This potential for higher uranium mobility in the oxidized zone is the reason for focusing on this area with reactive transport modeling, as the oxidized zone poses a greater concern for meeting regulatory compliance (no change in groundwater quality at the aquifer exemption boundary). However, at a larger scale, post-ISR groundwater will eventually encounter the reducing zone along the southwestern side of the oxidized zone (Fig. 4).

Reactive Transport Modeling

Methods and Model Setup

The model area is designed to simulate a restored ISR zone that is upgradient from the oxidized side of the uranium roll front (Fig. 4). Reactive transport modeling uses a 1D column with PHREEQC (Parkhurst and Appelo 2013) to create the 1D model domain shown in Fig. 5 to represent the 2D area shown in Fig. 4. Groundwater flow is from left to right in Fig. 5 and in all of the subsequent graphs. PHREEQC models flow velocity by specifying the cell size and a number of cell-to-cell shifts with time. At the Dewey Burdock site, calculated groundwater flow velocities are 1.86 m/yr (6.1 ft/yr) in an upper unit and 2.23 m/yr (7.3 ft/yr) in a lower unit (Petrotek 2012). Modeling used an upper-bound estimate on groundwater flow velocity of 5 m/yr (16.4 ft/yr) to simulate maximum transport conditions. For convenience, each cell was specified as 5 m (16.4 ft) in length, with a cell-to-cell shift each year. For initial simplicity, no dispersion was added to any of the simulations.

The actual "flare area" where groundwater moves away from each injection well is unknown but was assumed to be 61 m (200 ft), or half the distance from an injection well to the nearest monitoring well. The actual flare area will depend upon the final well spacing design and necessary injection rates. The assumed total length of the restored ISR zone is meant to include the injection and production well area, plus the flare area. The resulting distance from the end of the restored zone to the monitoring well ring is 61 m (200 ft) with a total proposed distance of 122 m (400 ft) from the nearest injection wells (Powertech 2008). Given the uncertainties in the actual flare area and the actual distance across the whole ISR production zone, 100 m is a convenient distance for the width of the restored area, with approximately another 100 m to the aquifer exemption boundary, which is proposed to be 36.6 m (120 ft) beyond the monitoring well ring (Powertech 2008). An additional 100 m distance was added to the 1D model domain to allow for longer-term downgradient transport. The number of cells, dimensions, overall model domain,

and locations of the monitoring well ring and the aquifer exemption boundary are summarized in Fig. 5. While these dimensions are specified in order to have distances on the 1D simulations that are similar to distances at the proposed Dewey Burdock ISR site, dimensional changes for any future modeling with different site conditions are easily adjusted.

As groundwater in each cell moves to the next cell, that water interacts with the solid phase specified in the next cell. For these reactions, the PHREEQC database was modified to include the calcium/magnesium uranyl carbonate complexes reported by Dong and Brooks (2006) and the recently updated uranium thermodynamics by Guillaumont et al. (2003). The full database is provided with the supplemental material in Johnson et al. (in review). For the base case simulations, no reactions were simulated in the restored ISR zone, and the downgradient zone included only sorption reactions (Fig. 5). Incoming groundwater at the left side of the 1D column used “background” groundwater. Since the proposed model domain does not have any true background groundwater quality data, the “background” groundwater uses well 684 within another ore zone (Johnson 2012). Because of the lack of oxygen, exploration holes that were converted to monitoring wells in and around the ore zone (upgradient and downgradient) have very similar groundwater quality along with low dissolved uranium concentrations (Johnson 2012). They are therefore reasonable proxies for typical background groundwater. No uranium was included in the background groundwater included in the simulations. Background groundwater was also used as the initial groundwater in the downgradient zone (Fig. 5). The final groundwater quality in the restored ISR zone is unknown. Based on the authors’ discussions with uranium recovery companies, 0.2 mg/L of dissolved uranium was added to the background groundwater to represent a reasonable restored-zone groundwater.

Sorption batch tests were completed to provide information on the downgradient sorption away from the restored ISR zone. The methods and final sorption parameters for three core samples are provided in Johnson et al. (in review), which provides total bulk uranium sorption parameters that are independent of uranium sorption on individual mineral assemblages. Core sample identification numbers are the same as those used in several previous studies (Johnson et al. [in review]; Johnson et al. 2013; Johnson 2012, and Powertech 2008, 2009). The final sorption parameters from Johnson et al. (in review) are used directly in the 1D PHREEQC simulations using the generalized composite surface complexation approach of Davis et al. (2004). Since these simulations are only in the oxidized zone, uranium is considered to remain soluble, and uranium precipitation reactions are not evaluated. We recognize that three samples are not sufficient for adequate predictions, and the resulting simulations are meant to assist in process understanding and provide an appropriate method for reactive transport modeling and future data collection.

Base Case Simulations

Predictive reactive transport simulations are shown for samples 11-14C-4 and 11-16C-2 along the 1D column (Fig. 6A and 6C) and at the monitoring well ring for 300 years (Fig. 6B and 6D). The monitoring well ring is at the 161 m distance in the 1D column. As discussed in Johnson et al. (in review), sample 11-16C-2 has a higher sorption capacity than sample 11-14C-4, providing dramatically different results in the predictions. Plots of simulations from sample 11-14C-5 are not provided because the sorption capacity of that sample at the 0.2 mg/L uranium concentration is essentially the same as 11-14C-4 (Johnson et al. [in review]). However, sample 11-14C-5 would provide a greater sorption capacity than 11-14C-4 at

higher uranium concentrations, as the sorption curves for these two samples are not the same at higher uranium concentrations (Johnson et al. [in review]).

In Fig. 6, the red line and square symbols indicate the transport of the 0.2 mg/L uranium left in the restored zone without any sorption (conservative transport). The blue line with diamond symbols represents uranium transport using the sorption parameters determined from the sorption batch tests in Johnson et al. (in review). At 30 years, much of the uranium is still very close to the end of the restored zone (at 100 m, Figs. 6A and 6C). This occurs because equilibrium sorption from the restored ISR zone groundwater with 0.2 mg/L has added uranium onto the aquifer solids. At 30 years, the restored zone water is at 150–250 m, and the equilibration of the background groundwater with the uranium-loaded solids in the 100–150 m distance creates the uranium concentrations seen in Figs. 6A and 6C. Through time at the monitoring well ring, the mass of uranium in the groundwater is spread out due to continual sorption/desorption processes, and the maximum peak concentration is reduced (Fig. 6B). If dispersion is added, this peak spreads out even more and has a lower peak concentration. For simplicity in comparing changes due to geochemical differences, dispersion was not added to any of the presented uranium transport predictions. For sample 11-16C-2, with stronger sorption, uranium is not detected at the monitoring well ring until after approximately 225 years due to continual sorption/desorption processes that create a retardation effect.

To evaluate the influence of calcite and possible errors in pH measurements, the following sections add slight differences to the base case simulations. These additional simulations provide sensitivity analysis that bound the range of reasonable uranium transport predictions. Such analyses should always be included as an integral part of any reactive transport modeling.

Simulations with Calcite Equilibrium

To evaluate the influence of reaction assumptions, the simulations discussed in the previous section and shown in Fig. 6 were redone with calcite equilibrium throughout the column. In the original simulations, the groundwater saturation index was -0.14 , or slightly undersaturated. This saturation index is well within potential analytical error. While the addition of calcite equilibrium is a small change in the groundwater chemistry, the predictive model is quite different (Fig. 7). In Fig. 7, the original simulations (with sorption, blue line, diamond symbol) and the conservative uranium transport (no sorption, red line, square symbol) are the same as shown in Fig. 6. The additional simulation with calcite equilibrium (with calcite, green line, triangle symbol) shows an increase in uranium mobility. This increased mobility is due to a decrease in sorption because of the additional amount of calcium uranyl carbonate complexes in solution created by a slight increase in calcite dissolution. These complexes keep uranium in solution, similar to the uranium ISR process, with the addition of complexing agents like carbon dioxide or sodium bicarbonate.

Simulations with pH Change Throughout the Column

To test prediction sensitivity with possible analytical error, the base case simulation for sample 11-14C-4 (Fig. 6A and 6B) was redone with a 5% increase in the measured pH (Fig. 7A and 7B) and a 5% decrease in the measured pH (Fig. 7C and 7D). The pH change was applied to the groundwater throughout the column and for any incoming background groundwater. The 5% increase in pH changes the pH from 6.78 to 7.12, and a 5% decrease in pH makes the value 6.44. The results in Fig. 7 indicate that the slight

change in pH has a dramatic influence on uranium mobility. In the PHREEQC output, the higher pH values increase the amount of calcium uranyl carbonate complexes in solution and decrease the amount of uranyl ion on the sorption surface, both of which increase uranium mobility. The reverse is true for the pH decrease. Further examination of the output indicates that the pH change provides a strong influence on the amount of uranyl ion in solution due to a change in the distribution of uranium complexes.

Simulations with Different pH Changes in the Restored and Background Zones

Given the pH sensitivity shown in Fig. 8 and discussed in the previous section, a final simulation was done using a lower pH in the restored zone (pH = 6) and a 5% increase in pH for the background groundwater. The results at 30 years (Fig. 9A) show a zone with uranium concentrations that are even higher than the original concentration of 0.2 mg/L uranium. At the monitoring well ring (Fig. 9B) between about 40 to 75 years, the uranium spike still reaches a peak of 0.225 mg/L. The reason for these predictions is an increase in sorption with the lower pH in the restored zone. Later in time, the higher pH in the background groundwater creates a larger desorption influence. Because of the large amount of sorbed uranium, the desorption influence creates higher uranium concentrations in groundwater than the original amount left in the restored zone.

The simulations for Figs. 9A and 9B did not include calcite equilibrium. Figs. 9C and 9D show the results when equilibration with calcite is assumed throughout the column. These simulations are probably more realistic, since at least some calcite is often present in many aquifers. The measured calcite amount from cores in the Burdock area is 0.15% calcite by weight (Johnson et al. 2013). These simulations show that uranium is more mobile in the restored zone water that has lower pH (Figs. 9C and 9D, areas under the no-sorption curve). This is due to the initially lower pH dissolving more calcite and creating more uranium complexes in solution. When the background groundwater with a 5% pH increase is allowed to come to equilibrium, calcite is precipitated, and subsequently there are fewer uranium complexes in solution. As the background groundwater moves into the column, this water establishes a new sorption curve (Figs. 9C and 9D, areas not underneath the no-sorption curve). The addition of calcite in this case demonstrates the need for quantitative mineralogy in the restored and the downgradient zone in addition to understanding the groundwater geochemistry.

Key Findings

These simulations demonstrate the high sensitivity in the predictions to very subtle changes in groundwater geochemistry, specifically pH and calcite equilibrium. However, based on the prediction differences in Fig. 6 for the two different samples, heterogeneity in the aquifer is also a very important issue, independent of any modeling assumptions. The next sections discuss additional data needs and provide an overall data collection guide. These sections provide guidance for reducing large prediction ranges with the most appropriate and more accurate data. However, the prediction difference based on overall heterogeneity will still remain.

Additional Data Needs

For this study, only three proxy core samples were available. More thorough reactive transport modeling would require actual downgradient core from multiple intervals. Sample intervals should be selected on the basis of the downhole geology. In addition, because of the limited number of calibration points for the

batch sorption tests, all of the sorption parameters could not be independently estimated (Johnson et al. [in review]). Additional calibration points could include additional uranium concentrations and additional geochemical conditions, such as changing pH, alkalinity, calcium, and carbon dioxide concentrations similar to the procedures of Davis et al. (2004). In addition to providing increased confidence in the calibration efforts, these additional data can provide actual confirmation of the sensitivity of uranium mobility with changing geochemistry.

Batch sorption tests provide adequate information for equilibrium conditions (Johnson et al. [in review]), but column studies can provide more realistic groundwater flow scenarios, where the addition of kinetic rates and rate-limited sorption might be necessary. Column tests can provide additional calibration data for reactive transport simulations beyond the equilibrium batch tests. Column tests should also include variations in uranium concentrations along with changing pH, alkalinity, and concentrations of calcium and carbon dioxide. Such tests can also provide data for sensitivities in uranium mobility with changes in geochemistry. Whether or not column tests could provide all of the necessary uranium sorption parameters without batch tests is an area for additional research.

The best calibration for reactive transport models at uranium ISR sites would be a pilot field study. The injection of post-restoration water into the downgradient zone would provide the most realistic information on uranium mobility. However, such a test also carries the risk of losing some of the injection water. A more likely scenario is an injection of post-restoration water from a restored ISR well field into a newly developed well field after the aquifer exemption has been approved. Presuming the new well field has not been turned on, any field test with injection, withdrawal, or natural flow testing of post-restoration water will be overprinted once the well field is activated.

Given the high sensitivity of reactive transport modeling results to pH, very accurate background and post-restoration groundwater geochemistry are required. Variations in space and time for these waters should be thoroughly evaluated, in addition to an evaluation of any analytical errors. Although not tested in this work, the evolution of background groundwater as it flows into the restored zone should also be evaluated. Over time, as the background groundwater flows into the restored ISR zone, the geochemistry of the background groundwater may change depending on the final mineralogy of the restored ISR zone.

General Data Collection Guide

In this data collection guide for reactive transport modeling at uranium ISR sites, it is assumed that thorough overall site characterization has already been completed. Such assumed characterization would include overall site geology and hydrogeology, ore locations, groundwater flow directions and velocities, and other relevant parameters. Specific modeling codes are not specified, but the use of the latest thermodynamic data for uranium speciation is necessary (Johnson and Tutu 2013). In order to proceed with reactive transport modeling (step 7 below), additional characterization data should include core analyses (steps 1–3) and sorption testing (steps 4–6) as listed below.

1. Collect representative downgradient core at multiple intervals with depth to characterize quantitative mineralogy (especially important for calcite).
2. Collect representative core in the restored zone at multiple intervals with depth to characterize quantitative mineralogy (especially important for calcite).

3. Contact the restored zone core in a column with background groundwater to produce an evolved background groundwater in the restored zone.
4. Conduct batch sorption and column tests using the downgradient core with the final restoration groundwater and evolved background groundwater to determine sorption parameters and possible mineral dissolution/precipitation reactions.
5. In the batch and column tests, use variable uranium concentrations and geochemical conditions that bracket the observed variations in field data in and around the restored well field.
6. Conduct field pilot tests, if possible.
7. Conduct reactive transport modeling with parameters and information derived from steps 1–6.

The addition of an evolved background groundwater is necessary to confirm whether the newly restored zone geochemistry will change the chemistry of the incoming background groundwater. For the Dewey Burdock modeling, such data are not available, since no ISR has occurred. Most of steps 1–7 above can be completed before uranium ISR begins, but some steps, such as collection of restored zone core and restored zone groundwater, need to occur after restoration is complete.

Batch sorption tests are adequate for equilibrium sorption parameters, but kinetic rates or dual domain conditions will need to be evaluated using column tests. In addition, column tests will likely improve transport modeling parameters that influence long-term concentration tailing effects. Temporarily stopping the flow in the column tests to evaluate concentration rebound is a critical test in evaluating whether the column is in equilibrium with the injection fluid. Field pilot tests would provide the best input parameters for reactive transport modeling, but they may not be feasible because of regulatory requirements and cost.

All of the above steps relate to providing adequate calibration data for rock/water interactions in a post-ISR scenario. Understanding the mineralogy of the downgradient and restored zones is a key element in providing the appropriate groundwater interactions with a series consisting of (1) restored zone water, (2) evolved background groundwater within the restored zone, and (3) background groundwater. As seen from the simulations related to the Dewey Burdock site, understanding the geochemistry of the water and solid phases in all of these zones under various conditions is critical. Appropriate laboratory testing through batch sorption and column testing can provide critical calibration data for predictive reactive transport models and provide bounding information on parameter sensitivities.

While the focus of this paper has been on the oxidized zone of a uranium roll-front formation, these procedures are just as applicable for evaluation of the reduced side. If a reducing zone is being evaluated, sampling and testing should be done in anoxic conditions with a focus on the amount of available reductants (e.g., organic carbon and pyrite), and the potential for uranium precipitation under reducing conditions should also be evaluated. Examination of mineral dissolution/precipitation reactions will require solid-phase analyses of the post-batch and post-column test material in order to identify uranium concentration reductions as being related to sorption or mineral precipitation.

Reactive transport modeling predictions (1D/2D/3D) can be done using appropriate interactions with the known mineralogy and the calibrated sorption parameters from batch and column testing. Additional interactions could include reactions such as mineral dissolution and precipitation, cation exchange, and redox changes. The inclusion of these additional reactions will need to be evaluated from the quantitative mineralogy results. Batch and column test results may confirm the need for any additional reactions but

may not provide direct evidence for these reactions. The final selection of the modeling code, number of dimensions, and combinations and locations of rock/water interactions will be site specific and based on available data and analytical results. The majority of efforts in such evaluations are in the tests to get appropriate model input parameters. Since no contaminant plume exists (and may never exist), the reactive transport modeling efforts are purely forward simulations with no additional calibration data being available until longer-term monitoring occurs.

Any modeling efforts should continually evaluate prediction ranges based on analytical uncertainties, natural heterogeneity (solid and water), and calibration uncertainties. These uncertainties can continue to be reduced as additional data become available. In addition, changes in overall rock/water interactions and updates to the conceptual model should be a continual process with any additional data. For example, as with the Dewey Burdock simulations, the final geochemistry of groundwater in the restored zone is not known. However, if reactive transport models have been completed for preliminary predictions, the true geochemistry of the restored groundwater can be entered, and transport simulations can be continually repeated. This will allow for continual evaluations of restoration progress, including evaluations of reasonable end points for restoration that will meet compliance at the aquifer exemption boundary. Longer term, such modeling efforts can continue to be an iterative process between modeling and data collection. Modeling results can assist in designing an appropriate monitoring network, and the data from such monitoring can be fed back into subsequent model updates.

Conclusions

Current regulations in the United States specifically state that groundwater quality should not be influenced downgradient from uranium ISR sites. However, longer-term downgradient monitoring has not been required at past ISR sites. Reactive transport modeling for the proposed Dewey Burdock uranium ISR site shows that sorption processes, even in oxidized bedrock, can provide significant natural attenuation of uranium. However, uncertainties due to heterogeneity, analytical error, and calibration error can produce large prediction ranges. Given these high sensitivities, accurate data on solid-phase and groundwater geochemistry are critical. In addition, batch and column testing with multiple uranium concentrations and variations in geochemical conditions can provide added calibration points to potentially decrease the reactive transport prediction ranges.

To provide a more consistent method for reactive transport modeling at uranium ISR sites, the data collection guide provides a more standard approach to evaluate downgradient transport. This data collection focus is on thorough solid- and water-phase measurement to understand rock/water interactions and provide appropriate input parameters for reactive transport modeling. This information can be used during restoration to evaluate whether restoration targets provide adequate protection of downgradient groundwater and can provide information on whether any proposed alternate concentration limits are reasonable.

While reactive transport modeling uncertainties can be reduced through careful evaluation of modeling assumptions, analytical errors, and calibration uncertainties; aquifer heterogeneities are difficult to fully determine in three dimensions. Therefore, any reactive transport model will never be a full representation of reality and will require some level of appropriate downgradient monitoring in the future. Reactive transport modeling provides predictive concentration ranges with distance that can be used to improve the design of monitoring networks. In turn, these monitoring networks can be used iteratively with the

modeling, adding calibration data through time to improve the modeling efforts and reduce the modeling uncertainties.

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References

- Bethke CM, Brady PV (2000) How the K_d approach undermines ground water cleanup. *Ground Water* 38(3): 435–443
- Borch T, Roche N, and Johnson TE (2012) Determination of contaminant levels and remediation efficacy in groundwater at a former in situ recovery uranium mine. *J Environ Mon* 14(7): 1814–1823.
- Curtis GP, Kohler M, Davis JA (2009) Comparing approaches for simulating the reactive transport of U(VI) in ground water. *Mine Water and the Environment* 28: 84–93
- Davis JD, Meece DE, Kohler M, and Curtis GP (2004) Approaches to surface complexation modeling of uranium(VI) adsorption on aquifer sediments. *Geochim Cosmochim Acta* 68(18): 3621–3641
- Dong W, Brooks SC (2006) Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) using anion exchange method. *Environ Sci Technol* 40:4689–4695
- EPA (2011) Considerations related to post-closure monitoring of uranium in-situ leach/in-situ recovery (ISL/ISR) sites, draft technical report. US Environmental Protection Agency Office of Air and Radiation Radiation Protection Division, June (<http://www.epa.gov/radiation/docs/tenorm/post-closure-monitoring.pdf>)
- EPA (2012a) Advisory review of considerations related to post-closure monitoring of uranium in-situ leach/in-situ recovery (ISL/ISR) sites, draft technical report. US Environmental Protection Agency Office of Air and Radiation, Radiation Protection Division, February. [http://yosemite.epa.gov/sab/sabproduct.nsf/964968D9229863A0852579A7006EC71A/\\$File/EPA-SAB-12-005-unsigned.pdf](http://yosemite.epa.gov/sab/sabproduct.nsf/964968D9229863A0852579A7006EC71A/$File/EPA-SAB-12-005-unsigned.pdf)
- EPA (2012b) Response to advisory review of considerations related to post-closure monitoring of uranium in-situ leach/in-situ recovery (ISL/ISR) sites, draft technical report, June. [http://yosemite.epa.gov/sab/sabproduct.nsf/0/964968d9229863a0852579a7006ec71a/\\$FILE/EPA-SAB-12-005_Response_06-12-2012.pdf](http://yosemite.epa.gov/sab/sabproduct.nsf/0/964968d9229863a0852579a7006ec71a/$FILE/EPA-SAB-12-005_Response_06-12-2012.pdf)
- Guillaumont R, Fanghanel T, Fuger J, Grenthe I, Neck V, Palmer D, Rand MH (2003) Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier, Amsterdam

Hall SM (2009) Groundwater restoration at uranium in-situ recovery mines, south Texas coastal plain. US Geological Survey open-file report 2009-1143, 32 pp. <http://pubs.usgs.gov/of/2009/1143/>

Harshman EN (1974) Distribution of elements in some roll-type uranium deposits. In: Proceedings from the symposium on the formation of uranium ore deposits, Athens, Greece. May 6, IAEA-SM-183/4, pp 169–183

Hobday DK, Galloway WE (1999) Groundwater processes and sedimentary uranium deposits. *Hydrogeology Journal* 7: 127–138

Johnson RH (2012) Geochemical data from groundwater at the proposed Dewey Burdock uranium in-situ recovery mine, Edgemont, South Dakota. US Geological Survey Open-File Report 2012-1070, 11 pp <http://pubs.usgs.gov/of/2012/1070/>

Johnson RH, Diehl SF, Benzel WM (2013) Solid-phase data from cores at the proposed Dewey Burdock uranium in-situ recovery mine near Edgemont, South Dakota. US Geological Survey Open-File Report 2013-1093, 13 pp. <http://pubs.usgs.gov/of/2013/1093/>

Johnson RH, Tutu Hlanganani (2013) Reactive transport modeling at uranium in situ recovery sites: uncertainties in uranium sorption on iron hydroxides. In: Brown A, Figueroa L, and Wolkersdorfer (Eds), *Reliable Mine Water Technology*, Vol I: 377–383; Denver, Colorado, USA (Publication Printers) http://www.imwa.info/docs/imwa_2013/IMWA2013_Johnson_417.pdf

Johnson RH, Truax R, Lankford D, and Stone J (in review) Sorption testing and generalized composite surface complexation models for the determination of uranium sorption parameters at a proposed uranium in-situ recovery site, *Mine Water and the Environment*

NRC (2009) Generic environmental impact statement for in-situ leach uranium milling facilities, US Nuclear Regulatory Commission, NUREG-1910, vols 1 and 2

NRC (2014) Environmental Impact Statement for the Dewey-Burdock project in Custer and Fall River counties, South Dakota, Supplement to the generic environmental impact statement for in-situ leach uranium milling facilities. US Nuclear Regulatory Commission, NUREG-1910, Supplement 4, vols 1 and 2, Final Report. NRC ADAMS Accession Number: ML14024A477 and ML14024A478 (<http://pbadupws.nrc.gov/docs/ML1402/ML14029A406.html>)

Parkhurst DL, Appelo CAJ (2013) Description of input and examples for PHREEQC version 3. A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey Techniques and Methods, book 6, chap. A43, 497 pp. Available at <http://pubs.usgs.gov/tm/06/a43/>

Petrotek (2012) Numerical modeling of hydrogeologic conditions, Dewey-Burdock project, South Dakota, Powertech Dewey-Burdock project Fall River and Custer Counties, SD, February, ([
HYPERLINK "<http://pbadupws.nrc.gov/docs/ML1206/ML12062A096.pdf>"])

Powertech (2008) Dewey-Burock project class III underground injection control permit application to the US EPA Region 8, updated January 2013, <http://www2.epa.gov/region8/underground-injection-control> and <ftp://ftp.epa.gov/r8/DeweyBurdock/DBApplication.pdf>

Powertech (2009) Dewey-Burdock project, application for NRC uranium recovery license Fall River and Custer counties, South Dakota. Environmental report, Docket No. 040-09075, ML092870160 (<http://pbadupws.nrc.gov/docs/ML0928/ML092870160.html>)